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Gas Response of Oxide Semiconductor Film Devices under Control of Diffusion and Reaction Effects

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Abstract

Sensor response of film semiconductor gas sensors to reducing gas under control of diffusion and reaction effects can be formulated as a function of film thickness and Hatta number based on recent theory of the receptor function of small crystals. The bell shaped dependence of the response on temperature can also be derived theoretically.

Keywords: semiconductor, gas sensor, diffusion, reducing gas, size effect, oxide

1. Introduction

Response of semiconductor gas sensors to reducing gas is known to be influenced by diffusion and reaction effects (abbreviated as diffusion effects hereafter). For a film device, the phenomena have been analyzed by starting from a diffusion and reaction equation of the following form.[1, 2]

$$d P_A / d t = D_K d^2 P_A / dx^2 - k P_A \quad (1)$$

P_A is the partial pressure of target gas, A, t time, D_K Knudsen diffusion coefficient, x distance from the top surface of the sensing layer, and k rate constant. At the steady state, $d P_A / d t = 0$, and the resulting solution of (1) gives rise to the correlation between P_A and x. The resulting analyses have explained the actual dependence of response on thickness or temperature rather well.[2] However, these analyses can not always be justified because of the various assumptions used; even (1) remains to be verified. Recently we succeeded in deriving theoretically the sensor response free of the diffusion effects.[3-6] Theory can be extended to include the diffusion effects. This paper aims at doing this in order to strengthen the fundamental basis of semiconductor gas sensors.

2. Conditions of receptors verifying (1)

Sensor response originates from the receptor function of each constituent crystal (spherical one here). In air, oxygen is adsorbed ($O_2 + 2e = 2O^-$) to reach equilibrium, while target gas reacts with the adsorbates ($O^- + A = AO + e$) to reach steady state. These processes are concerted with a change in electronic state of the crystal. As the recent theory indicates, a tiny crystal finishes depletion of the conventional type (regional depletion) easily at lower partial

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pressure of oxygen (P_{O2}) to enter new type one (volume depletion).[3] On the basis of the simplest depletion model (abrupt model), surface density of oxygen adsorbates, $[O^-]$, and resistance normalized by that at flat band state, R/R_0, can be depicted as a function of $(K_{O2}P_{O2})^{1/2} / L_D$ for chosen reduced size n (= a /L_D), as shown in Figure 1. Here K_{O2}, L_D and a are equilibrium constant of oxygen adsorption, Debye length and grain radius, respectively. Importantly, $[O^-]$ is kept constant, while R/R_0 increases linearly, in the region of volume depletion. ($[O^-]$ changes slightly in the same region on more rigorous model, but such slight variations are neglected here for simplicity.)

This assures that $[O^-]$ can also remain constant even when small P_A is introduced provided that n and K_{O2} are sufficiently small and large, respectively. Under such a condition, the resistance under exposure to A, R_g, follows

$$R_g/R_0 = (3/n) \{(K_{O2}P_{O2})^{1/2} / L_D\}/ \{1 + b\ P_A\}^{1/2},\ b = 3k_A / (n\ k_{-1}N_dL_D) \quad (2)$$

$$R_a/R_g = \{1 + b\ P_A\}^{1/2} \quad (3)$$

if the diffusion effects are disregarded.[6] Here k_A and k-1 are rate constants of the surface reaction of A and the oxygen desorption, respectively, N_d is donor density of the crystals, and Ra is resistance in air.

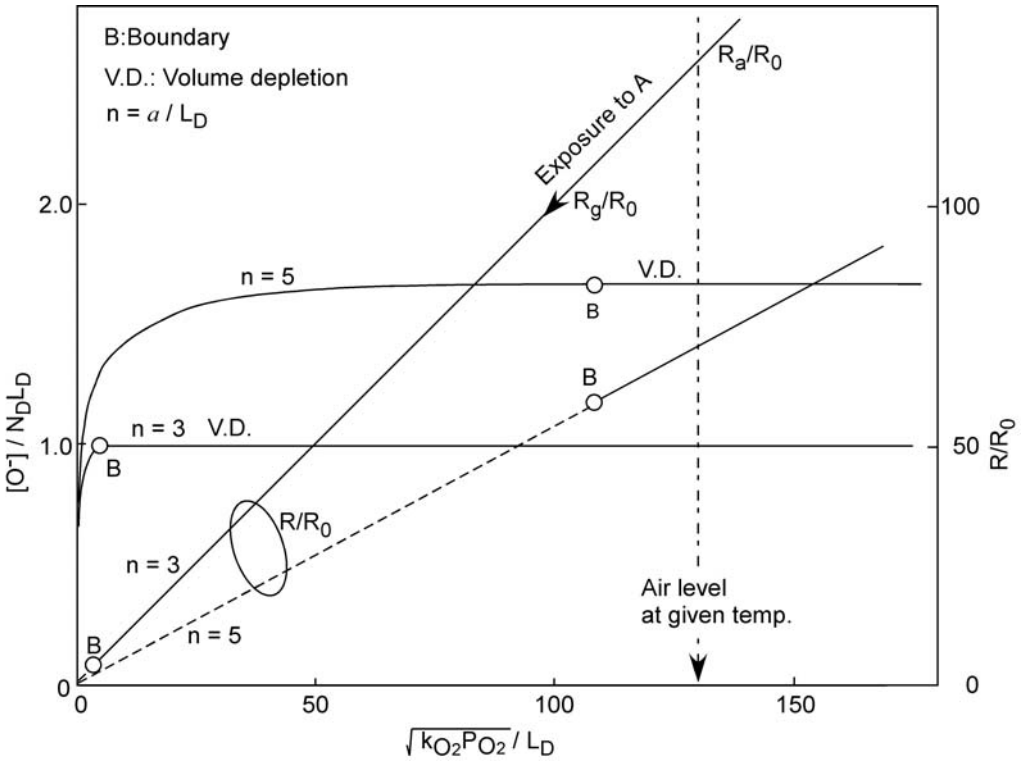

Fig. 1: $[O^-]$ and R/R_0 as correlated with $(K_{O2}P_{O2})^{1/2}/L_D$ for n = 3 or 5.

3. Depth profile of P_A

Under control of the diffusion effects, P_A becomes a function of depth (x) from the top surface, which is estimated as follows. As long as $[O^-]$ is constant, the rate of reaction of A per unit surface area of each grain, $k_AP_A[O^-]$, is linear to P_A. That is, (1) can hold if k is equated with $k_A[O^-]$ s / d , where s and d are specific surface area and bulk density of the sensing layer, respectively. The depth profile of P_A inside the film is thus given as follows.[2]

$$P_A(x)/P_{A,S} = \cosh ((L - x)\ (k/D_K)^{1/2}) / \cosh (L\ (k/D_K)^{1/2}) \quad (4)$$

$P_{A,S}$ is the value of P_A at x = 0, and L thickness of the film. The profiles are depicted for selected L by taking $(k/D_K)^{1/2}$ as a parameter in Figure 2. It is remarked that the volume depletion condition is narrowed as n increases or temperature increases (K_{O2} decreases). Outside of this condition, the second term of (1) becomes non-leaner to P_A, making the equation unsolvable mathematically.

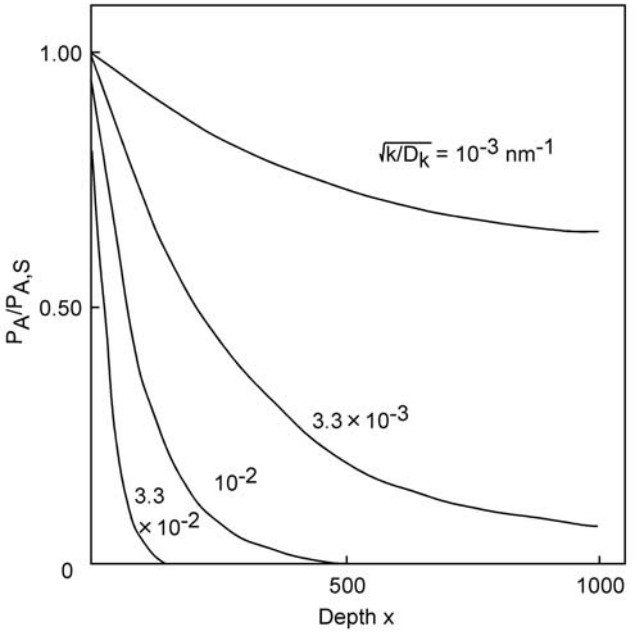

Fig. 2: Depth profiles of P_A for selected values of $(k/D_K)^{1/2}$ (film thickness 1000 nm).

4. Sensor response and its dependence on film thickness

Once P_A is known as a function of x under the volume depletion condition, sensor response of the whole film, S, can be evaluated by integrating normalized sheet conductance at x, which is given as reciprocal of (3).

$$S = R_a/R_g = (1/L)\int_0^L F(x)dx\,,\ F(x) = (1 + b\,P_A(x))^{1/2} \tag{5}$$

Figure 3 shows the correlation between S and L at b $P_{A,S} = 10^4$ for selected values of $(k/D_K)^{1/2}$. As shown in Figure 4, S can be generalized with Hatta number m (= $L(k/D_K)^{1/2}$) more smartly.

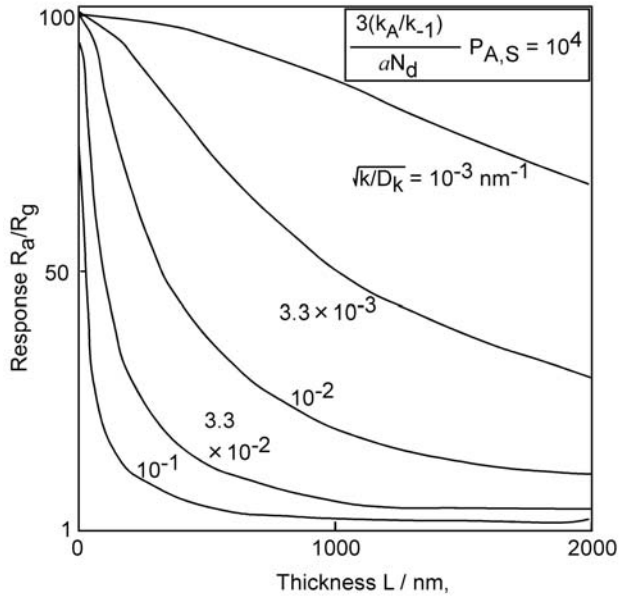

Fig. 3: Sensor response drawn as a function of film thickness L for various values of $(k/D_K)^{1/2}$ under a selected condition of $c_1P_{A,S} = 10000$.

5. Dependence on temperature

S is a function of two sets of constants ratios, k_A/ k_{-1} and k/D_K (see Figure 4). The former set determines the sensor response free of the diffusion and reaction effects, S_f, while the latter does its modulation by the same effects, $U = S/S_f$ (U is called utility factor). Either set is considered to grow sharply as temperature increases. In such a low temperature region where m and U are kept smaller than unity, S coincides with S_f and increases with increasing temperature (k_A control). In a sufficiently high temperature region, on the other hand, U diminishes far more sharply than S_f does on increasing temperature (U control). Thus one obtains a bell-shaped correlation between S and T as actually observed.

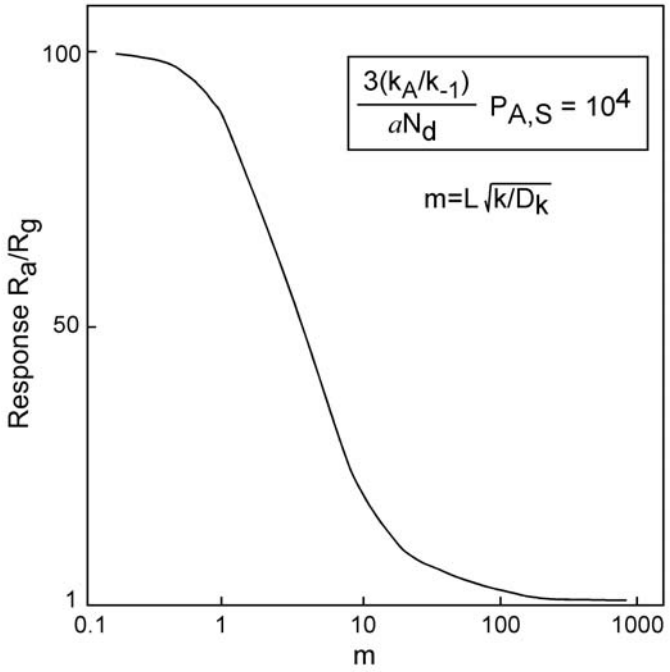

Fig. 4: Sensor response as correlated with Hatta number m.

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